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## (54) METHOD FOR ACTIVATING METAL OXIDE CATALYST

## (57)Abstract:

PURPOSE: To further enhance the activity of a metal oxide catalyst contg. Mo and/or V for a vapor phase catalytic oxidation reaction of hydrocarbon through a simple operation by subjecting the catalyst to acid treatment.

CONSTITUTION: A metal oxide catalyst contg. Mo and/or V for a vapor phase catalytic oxidation reaction of hydrocarbon is subjected to acid treatment. The atomic ratio of Mo to V in the metal oxide is preferably 0.1-2. The acid treatment is carried out by immersing the catalyst in an about 0.1-50wt.% aq. soln. of an inorg. or org. acid at room temp. to 90°C. After the acid treatment, the catalyst is separated from the acid soln. by a method such as filtration or centrifugal separation. The separated catalyst is usually washed with water in some degree, dried and used as a catalyst. The dried catalyst may be heated at about 100-700°C if necessary before use.

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**CLAIMS****[Claim(s)]**

**[Claim 1]** The activation method of the metal oxide catalyst characterized by carrying out acid treatment of the metal oxide catalyst containing the molybdenum and/or vanadium for a gaseous-phase catalytic-oxidation reaction of a hydrocarbon.

**[Claim 2]** The activation method of the metal oxide catalyst of a claim 1 that the metal oxide catalyst containing molybdenum and/or vanadium is characterized by drying, and calcinating and obtaining the solution or the slurry containing the compound of molybdenum and/or vanadium.

**[Claim 3]** The activation method of the metal oxide catalyst according to claim 1 or 2 characterized by carrying out acid treatment by the organic acid.

**[Claim 4]** The activation method of a metal oxide catalyst according to claim 1 to 3 that a metal oxide catalyst is characterized by what is expressed with the following empirical formula (1).

**[Formula 1]**  $M_a O_b V_b X_x O_n$  (1)

(In a formula (1), X expresses one or the element beyond it chosen from Te, Nb, Ta, W, Ti, aluminum, Zr, Cr, Mn, Fe, Ru, Co, Rh, nickel, Pd, Pt, Sb, Bi, B, In, and Ce.) when referred to as  $a = 1$ , it is  $b = 0.01-10$ ,  $x = 0-2.0$ , and  $n$  is determined by the oxidation state of other elements

**[Claim 5]** The activation method of a metal oxide catalyst according to claim 1 to 3 that a metal oxide catalyst is characterized by what is expressed with the following empirical formula (2).

**[Formula 2]**  $M_a O_b V_b T_e c Y_y O_n$  (2)

(In a formula (2), Y expresses one or the element beyond it chosen from Nb, Ta, W, Ti, aluminum, Zr, Cr, Mn, Fe, Ru, Co, Rh, nickel, Pd, Pt, Sb, Bi, B, In, and Ce.) when referred to as  $a = 1$ , it is  $b = 0.01-1.0$ ,  $c = 0.01-1.0$ ,  $y = 0.01-1.0$ , and  $n$  is determined by the oxidation state of other elements

**[Claim 6]** The activation method of the metal oxide catalyst according to claim 1 to 5 characterized by a metal oxide catalyst being a catalyst for manufacturing acrylonitrile by the gaseous-phase catalytic-oxidation reaction from a propane under existence of ammonia.

[Translation done.]

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**DETAILED DESCRIPTION**


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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the activation method of the metal oxide catalyst containing the molybdenum and/or vanadium for a gaseous-phase catalytic-oxidation reaction of a hydrocarbon.

[0002]

[Description of the Prior Art] Especially the metal oxide catalyst containing molybdenum and/or vanadium is industrially important in order to manufacture nitril, such as oxygenated organic compounds, such as manufacture of various kinds of organic compounds by the gaseous-phase catalytic-oxidation reaction of a hydrocarbon, an acrylic acid by the partial oxidation reaction of a hydrocarbon, and a maleic anhydride, or acrylonitrile by the catalytic-oxidation reaction of a hydrocarbon and ammonia, and a methacrylonitrile, especially.

[0003] Many examples of a report of the metal oxide catalyst containing molybdenum and/or vanadium are known. For example, the catalyst which contains molybdenum as essential element by the object for nitril manufacture by the catalytic-oxidation reaction of the alkane and ammonia of a hydrocarbon and a Mo-Bi-P system catalyst (JP,48-16887,A), The catalyst which was mixed mechanically and obtained the V-Sb-W system oxide and the Mo-Bi-Ce-W system oxide (JP,64-38051,A), A Mo-Ag-Bi-V system catalyst (JP,3-58961,A), a Mo-V-Sn-Bi-P system catalyst (JP,4-247060,A), A Mo-Cr-Te system catalyst (U.S. JP,5171876,B), Mo and Mn, The compound metal oxide catalyst which consists of elements, such as Co, (JP,5-194347,A), A Mo-V-Te system catalyst (JP,2-257,A, JP,5-148212,A, JP,5-208136,A), a Mo-Cr-Bi system catalyst (Japanese Patent Application No. No. 265192 [ four to ], Japanese Patent Application No. No. 305361 [ five to ]), a Mo-Te system catalyst (Japanese Patent Application No. No. 309345 [ five to ]), etc. are illustrated.

[0004] Moreover, although vanadium is included as an indispensable component, a V-Sb system catalyst (JP,47-33783,A, JP,50-23016,B, JP,1-268668,A, JP,2-180637,A), a V-Sb-U-nickel system catalyst (JP,47-14371,B), a V-Sb-W-P system catalyst (JP,2-95439,A), a V-W-Te system catalyst (Japanese Patent Application No. No. 18918 [ five to ]), etc. are illustrated as a catalyst whose molybdenum is not an indispensable component.

[0005] As the manufacture method of this metal group oxide, the following two methods are mainly raised. The 1st method is the method of enforcing the method of collecting solids, after carrying out the pyrogenetic reaction of the method of drying after preparing the solution or slurry of the water containing the composition element of a metallic oxide, or an organic solvent, or adjusting pH of a solution, and settling a solid, a solution, or the slurry and compounding the target metallic oxide, and calcinating the solid still more generally obtained, and making it into a catalyst.

[0006] The 2nd method is specified quantity [ every ] trituration and the method of mixing,

holding to an elevated temperature and preparing according to solid phase reaction about the oxide of the composition metallic element of a metallic oxide.

[0007]

[Problem(s) to be Solved by the Invention] It depends for the activity of a catalyst on the composition greatly. However, although the catalytic activity which optimized composition of a catalyst and was essentially excellent is expectable, sufficient catalytic activity cannot be discovered in very many cases by the manufacture method etc. In the catalyst which consists of the above compound metallic oxides especially, the manufacture operation is complicated and there is a problem that the catalytic activity expected by change of delicate manufacture conditions is not obtained with sufficient repeatability.

[0008]

[Means for Solving the Problem] As a result of continuing examination about the manufacture method of the metal oxide catalyst containing molybdenum and/or vanadium, taking the above-mentioned technical problem into consideration, by carrying out acid treatment of the metal oxide catalyst, a catalyst is activated, and this invention persons find out that the performance which was excellent in the alternative gaseous-phase catalytic-oxidation reaction of especially a hydrocarbon is shown, and reach this invention.

[0009] That is, the summary of this invention consists in the activation method of the metal oxide catalyst characterized by carrying out acid treatment of the metal oxide catalyst containing the molybdenum and/or vanadium for a gaseous-phase catalytic-oxidation reaction of a hydrocarbon. Hereafter, this invention is explained in detail. Although the catalyst which can be activated by this invention will not be limited especially if it is a metal oxide catalyst containing above molybdenum and/or above vanadium, it is a metal oxide catalyst which contains both molybdenum and vanadium as essential element preferably. the atomic ratio (V/Mo) of the molybdenum atom in a metallic oxide, and a vanadium atom -- usually -- 0.01-10 -- it is 0.1-2 preferably In order that this metallic oxide may usually raise the performance as a catalyst, various arbitrary metal components are contained, and the composition is expressed with the following empirical formulas (1).

[0010]

[Formula 3]  $M_a O_b X_x O_n$  (1)

(In a formula (1), X expresses one or the element beyond it chosen from Te, Nb, Ta, W, Ti, aluminum, Zr, Cr, Mn, Fe, Ru, Co, Rh, nickel, Pd, Pt, Sb, Bi, B, In, and Ce.) when referred to as  $a=1$ , it is  $b=0.01-10$ ,  $x=0-2.0$ , and  $n$  is determined by the oxidation state of other elements

[0011] Moreover, in the above-mentioned metal oxide catalyst, especially the catalyst that contains a tellurium as an indispensable component in addition to molybdenum and vanadium is desirable. This molybdenum-vanadium-tellurium system catalyst By having the catalytic activity which was excellent also in the partial oxidation reaction of a reactant low alkane also in the hydrocarbon, and choosing the conditions of a gaseous-phase catalytic-oxidation reaction suitably manufacture (JP,2-257,A and JP,5-148212,A --) of nitril, such as acrylonitrile Manufacture of alpha, such as JP,5-208136,A and an acrylic acid, and beta-unsaturated carboxylic acids (Japanese Patent Application No. No. 12616 [ five to ]) anhydrous unsaturation carvones, such as Japanese Patent Application No. No. 153651 [ five to ], or a maleic anhydride, -- it can use for various reactions, such as manufacture (Japanese Patent Application No. No. 17560 [ five to ]) of acids, and especially the effect of activation by the acid treatment in this invention is remarkable Composition of this molybdenum-vanadium-tellurium system metallic oxide is expressed with the following empirical formulas (2).

[0012]

[Formula 4]  $M_a O_b T_e c Y_y O_n$  (2)

(In a formula (2), Y expresses one or the element beyond it chosen from Nb, Ta, W, Ti,

aluminum, Zr, Cr, Mn, Fe, Ru, Co, Rh, nickel, Pd, Pt, Sb, Bi, B, In, and Ce.) the time of being referred to as  $a=1$  --  $b=0.01-1.0$  -- desirable --  $0.1$  to  $0.6$ , and  $c=0.01-1.0$  -- desirable --  $0.05$  to  $0.4$ , and  $y=0.01-1.0$  -- desirable --  $0.1$  to  $0.6$  -- it comes out, and it is and  $n$  is determined by the oxidation state of other elements

[0013] Although it can be used as a catalyst even if the metallic oxide of the above-mentioned formula (1) and (2) is independent, you may carry out acid treatment of this invention in the state of the mixture which could use as a catalyst the mixture which used one or more sorts of oxides of Si, aluminum, Zr, Ti, and an alkaline-earth-metal oxide as the support component, for example, contained the support component about 1 to 90% of the weight.

[0014] As a raw material of a metallic oxide, the carboxylate of molybdenum, vanadium, and other arbitrary metal components, a carboxylic-acid ammonium salt, an ammonium-halide salt, an oxide, a halogenide, a hydro acid, acetylacetonato, an alkoxide, a halogenide, etc. can be used. Especially limitation does not have the manufacture method of a metallic oxide, and two are in the Lord of the method of preparing as mentioned above from the solution or slurry of the raw material water of a metallic oxide, or an organic solvent, and the method of mixing the raw material of a metallic oxide and preparing according to elevated-temperature solid phase reaction. However, it dries and the method of calcinating is [ after preparing the solution or the slurry which contains the compound of the former method especially molybdenum, and/or vanadium in that the catalyst which was more excellent in activity is acquired ] desirable.

[0015] this invention is characterized by carrying out acid treatment of the metal oxide catalyst containing the above molybdenum and/or vanadium, and activating a metal oxide catalyst further. It is aimed at the metallic oxide newly prepared by the above methods as a metal oxide catalyst which performs this acid treatment, and also let the metallic oxide to which it was already used at the reaction and catalytic activity fell be an object.

[0016] As the method of acid treatment, contact processing of the metal oxide catalyst is carried out at an acid solution. For example, immersing processing of the metal oxide catalyst is carried out at room temperature -90 degree C into solution of about 0.1 - 50 % of the weight of usual [ of an inorganic acid or an organic acid ]. In addition, in case acid treatment is performed depending on the case, you may carry out trituration processing of the metal oxide catalyst. As an inorganic acid used for acid treatment, a hydrochloric acid, a sulfuric acid, a nitric acid, a phosphoric acid, a boric acid, etc. are effective. Moreover, as an organic acid, although an about one to 12-carbon number aliphatic carboxylic acid and an aromatic carboxylic acid are illustrated, aliphatic polybasic acid, such as oxalic acid, a citric acid, a tartaric acid, a malonic acid, a succinic acid, and a maleic acid, is especially effective. Even if these acids are independent, they may use two or more sorts, mixing arbitrarily.

[0017] Although the detail of the reason a catalyst is further activated by this acid treatment is not clear, it is presumed that the chemical state of the front face of a catalyst or the interior changes with acid treatment, dissolution removal is carried out, a physical property like a surface area is improved, or the component leading to the side reaction which is not desirable for a reaction is depended on a front face advantageous to the activity of a reaction and selectivity appearing etc.

[0018] After carrying out acid treatment, a metal oxide catalyst is separated from an acid solution by methods, such as filtration or centrifugal separation. And a metal oxide catalyst is usually washed to some extent with water, and subsequently, after drying, it is used as a catalyst. Moreover, if needed, since it heat-treats in about 100-700 degrees C, you may use it as a catalyst. The metal oxide catalyst containing the molybdenum and/or vanadium which were activated by the above method is used for manufacture of the organic compound by the gaseous-phase catalytic-oxidation reaction of a hydrocarbon. Although the gaseous-phase catalytic-oxidation reaction of the hydrocarbon in this invention carries out gaseous-phase

catalytic reaction of the hydrocarbon to oxygen, a reaction for which ammonia, a steam, etc. are made to exist in the system of reaction other than oxygen is also included, and it is applied to manufacture of various kinds of organic compounds, such as an oxygenated organic compound, a dehydrogenation organic compound, and nitril. And the service condition of the activation catalyst in this invention should just already make it the same conditions as a well-known reaction condition in each catalyst system, and can obtain the target product by high selectivity and high yield more as compared with the case where the catalyst which is not activated is used.

[0019] As a hydrocarbon of a reaction raw material, an about three to eight-carbon number alkane or an alkene, an about six to 12-carbon number aromatic hydrocarbon, etc. are mentioned. Manufacture of the nitril according to the gaseous-phase catalytic-oxidation reaction of an alkene or an alkane, and ammonia as the example of a reaction (For example, manufacture the acrylonitrile from a propylene or a propane, and ammonia) The manufacture alkane of the acrylonitrile from an isobutene or an isobutane, and ammonia, or the unsaturation aldehyde by the partial oxidation reaction of an alkene, manufacture (for example, the acrolein from a propane or a propylene --) of a unsaturated carboxylic acid Manufacture of an acrylic acid, an isobutane, or the methacrolein from an isobutene, Manufacture of a methacrylic acid, the oxidization dehydrogenation of a saturation carboxylic acid (For example, manufacture of an isobutyric acid to a methacrylic acid), the oxidization dehydrogenation of a hydrocarbon There is manufacture (for example, manufacture of the maleic anhydride from the manufacture, the butane, or the butene of phthalic anhydride from naphthalene or a xylene) of the acid anhydride by (for example, manufacture of the butadiene from a butene) and the partial oxidation reaction of various hydrocarbons etc.

[0020] furthermore, the conditions of the gaseous-phase catalytic-oxidation reaction of the hydrocarbon in the molybdenum-vanadium-tellurium system catalyst shown by the above-mentioned formula (2) which has a remarkable effect especially are boiled, attached and stated by the activation method of this invention This catalyst usually has comparatively the property of 500 degrees C or less that the partial oxidation activity of an alkane is high, under low temperature as compared with the metal oxide catalyst for other gaseous-phase catalytic-oxidation reactions. gas-space-velocity simian virus [ in / gaseous phase reaction / in the gaseous-phase catalytic-oxidation reaction using this catalyst, 300-500 degrees C of reaction temperature are about 350-450 degrees C preferably, and ] -- 100-10000hr-1 -- \*\*\*\*\* under the pressurization of low degree, or reduced pressure although it is the range of 300-6000hr-1 preferably and a reaction can usually be carried out under atmospheric pressure . Moreover, inert gas, such as nitrogen, an argon, and helium, can be used as dilution gas for adjusting space velocity and oxygen tension. Although a reaction method can adopt both the fixed bed, the fluid bed, etc., since it is exothermic reaction, the fluid bed method is easier for control of reaction temperature.

[0021] This molybdenum-vanadium-tellurium system catalyst is effective in manufacture of the nitril by the gaseous-phase catalytic-oxidation reaction of an alkane and ammonia, especially manufacture of the acrylonitrile from a propane. this reaction \*\*\*\* -- about the selectivity of the acrylonitrile which the rate of the oxygen supplied to the system of reaction generates, it is important and oxygen shows high acrylonitrile selectivity in the range of the amount of 0.2-4 mol times especially to a propane Moreover, the range of the amount of 0.5-3 mol times is suitable for especially the rate of the ammonia with which a reaction is supplied to a propane.

[0022] An acrylic acid can be obtained by high yield by performing the gaseous-phase catalytic-oxidation reaction of a propane using the same molybdenum-vanadium-tellurium system catalyst. Although a propane and oxygen content gas are used as reaction material gas, it can be desirable to use a steam and it can raise the selectivity of an acrylic acid further with a

steam. As a mole fraction of material gas, it is : (propane) (oxygen):(steam) = 1:(1-5): (5-40) preferably.

[0023]

[Example] Although an example is given and this invention is hereafter explained further to a detail, this invention is not limited to these examples, unless the summary is exceeded. In addition, propane (%) and the invert ratio in the following examples and examples of comparison, acrylonitrile (%) and selectivity, and acrylonitrile yield (%) are respectively shown by the following formulas.

[0024]

[Equation 1] Yield (%) = (number of mols of number of mols / supply propane of generation acrylonitrile) x100 [ of invert ratio (%) = (number of mols of number of mols / supply propane of consumption propane) x100 acrylonitrile of a propane ] of selectivity (%) = (number of mols of number of mols / consumption propane of generation acrylonitrile) x100 acrylonitrile. [0025] example of comparison 1 empirical-formula  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.18}$  -- mixture (weight ratio 70:30) \*\* of On and  $\text{SiO}_2$  was prepared as follows 5.52kg of the Para ammonium-molybdate salts, 1.10kg of ammonium metavanadate salts, and 1.65kg of telluric acids were dissolved in warm water 22.7L, and uniform solution was prepared. Furthermore, 8.55kg of oxalic acid niobium ammonium solution whose concentration of silica-sol 15kg whose silica content is 20 % of the weight, and niobium is 0.659 mols/kg was mixed, and the slurry was prepared. Having supplied this slurry to the spray drier the speed for about 120ml/, and supplying the heated air, moisture was removed and it dried. At this time, the temperature for a core of a spray drier was about 160 degrees C. After heat-treating this dry matter at about 300 degrees C until the ammonia smell was lost, it calcinated at 600 degrees C among the nitrogen air current for 2 hours.

[0026] The reactor was filled up with 0.7g of metallic oxides prepared as mentioned above, the reaction temperature of 410 degrees C and space velocity simian virus were fixed to 880hr-1, gas was supplied by the mole ratio of propane:ammonia:air = 1:1.2:15, and the gaseous-phase catalytic-oxidation reaction was performed. A reaction result is shown in Table -1.

[0027] 100g of 110 % of the weight oxalic acid solution of examples was warmed at 50 degrees C, and it prepared in the example 1 of comparison here -- it held at 50 degrees C for 1.5 hours, stirring by adding 10g (weight ratio 70:30) of  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.18}$  mixture of On and  $\text{SiO}_2$  After cooling radiationally to a room temperature, filtration separation of the solid-state was carried out from this liquid. This solid-state was moved to another container, and 100ml of deionized water was added, and at the room temperature, stirring was performed for 5 minutes and it filtered. Furthermore, this washing operation was repeated 3 times. After drying at a room temperature, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The gaseous-phase catalytic-oxidation reaction was performed for a propane and ammonia on conditions like the example 1 of comparison using the metallic oxide which performed the above processing. A reaction result is shown in Table -1.

[0028] example of comparison 2 empirical-formula  $\text{Mo}_1\text{V}_{0.24}\text{Te}_{0.23}\text{Nb}_{0.12}$  -- the mixture (weight ratio 50:50) of On and  $\text{SiO}_2$  was prepared as follows 808.6g of the Para ammonium-molybdate salts, 128.6g of ammonium metavanadate salts, and 241.9g of telluric acids were dissolved in 3019ml of warm water, and uniform solution was prepared. Furthermore, silica-sol 5000g whose silica content is 20wt(s)%, and 1268g of oxalic acid niobium ammonium solution whose concentration of niobium is 0.435 mols/kg were mixed, and the slurry was prepared. Having supplied this slurry to the spray drier the speed for about 120ml/, and supplying the heated air, moisture was removed and it dried. At this time, the temperature for a core of a spray drier was about 160 degrees C.

[0029] After heat-treating this dry matter at about 300 degrees C until the ammonia smell was



lost, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The reactor was filled up with 1.0g of metallic oxides prepared as mentioned above, the reaction temperature of 410 degrees C and space velocity SV were fixed to 440hr<sup>-1</sup>, gas was supplied by the mole ratio of propane:ammonia:air = 1:1.2:15, and the gaseous-phase catalytic-oxidation reaction was performed. A reaction result is shown in Table -1.

[0030] 100g of 25 % of the weight oxalic acid solution of examples was warmed at 50 degrees C, and it prepared in the example 2 of comparison here -- it held at 50 degrees C for 1.5 hours, stirring by adding 10g (weight ratio 50:50) of Mo<sub>1</sub>V<sub>0.24</sub>Te<sub>0.23</sub>Nb<sub>0.12</sub> mixture of On and SiO<sub>2</sub>. After cooling radiationally to a room temperature, filtration separation of the solid-state was carried out from this liquid. This solid-state was moved to another container, and 100ml of deionized water was added, and at the room temperature, it stirred for 5 minutes and filtered. Furthermore, this washing operation was repeated 3 times. After drying at a room temperature, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The gaseous-phase catalytic-oxidation reaction was performed for a propane and ammonia on the same conditions as the example 1 of comparison using the metallic oxide which performed the above processing. A reaction result is shown in Table -1.

[0031] Although processing by oxalic acid solution was performed like example 3 example 2, the gaseous-phase catalytic-oxidation reaction of a propane and ammonia was performed on the same conditions as an example 2, without performing baking in the nitrogen air current after processing and dryness. A reaction result is shown in Table -1.

Except having made temperature of the oxalic acid solution of example 4 example 2 into 80 degrees C, the same processing as an example 2 was performed, and the gaseous-phase catalytic-oxidation reaction of a propane and ammonia was performed on the same conditions as an example 2. A reaction result is shown in Table -1.

[0032] It held at 70 degrees C for 1.5 hours, having warmed 100g of 55 % of the weight citric-acid solution of examples at 70 degrees C, and stirring by adding 10g of metallic oxides prepared in the example 2 of comparison here. After cooling radiationally to a room temperature, filtration separation of the solid-state was carried out from this liquid. This solid-state was moved to another container, and 100ml of deionized water was added, and at the room temperature, it stirred for 5 minutes and filtered. Furthermore, this washing operation was repeated 3 times. After drying at a room temperature, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The gaseous-phase catalytic-oxidation reaction was performed for a propane and ammonia on the same conditions as an example 2 using the metallic oxide which performed the above processing. A reaction result is shown in Table -1.

[0033] In 100g of 65 % of the weight tartaric-acid solution of examples, 10g of metallic oxides prepared in the example 2 of comparison was added, and it held at the room temperature with the stirring deed in it for 20 hours. After cooling radiationally to a room temperature, filtration separation of the solid-state was carried out from this liquid. This solid-state was moved to another container, and 100ml of deionized water was added, and at the room temperature, it stirred for 5 minutes and filtered. Furthermore, this washing operation was repeated 3 times. After drying at a room temperature, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The gaseous-phase catalytic-oxidation reaction was performed for a propane and ammonia on the same conditions as an example 2 using the metallic oxide which performed the above processing. A reaction result is shown in Table -1.

Except having used hydrochloric-acid solution 5% of the weight instead of the 5-% of the weight citric-acid solution of example 7 example 5, the same processing as an example 5 was performed, and the gaseous-phase catalytic-oxidation reaction of a propane and ammonia was performed on the same conditions as an example 5. A reaction result is shown in Table -1.

[0034] Except having used phosphoric-acid solution 5% of the weight instead of the 5-% of the

weight citric-acid solution of example 8 example 5, the same processing as an example 5 was performed, and the gaseous-phase catalytic-oxidation reaction of a propane and ammonia was performed on the same conditions as an example 5. A reaction result is shown in Table -1. Except having used it 100g of warm water instead of the 5-% of the weight oxalic acid solution of example of comparison 3 example 2, the same processing as an example 2 was performed, and the gaseous-phase catalytic-oxidation reaction of a propane and ammonia was performed on the same conditions as an example 2. A reaction result is shown in Table -1.

[0035] example of comparison 4 empirical-formula  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$  -- the mixture (weight ratio 50:50) of On and  $\text{SiO}_2$  was prepared as follows 3.94kg of the Para ammonium-molybdate salts, 0.784kg of ammonium metavanadate salts, and 1.18kg of telluric acids were dissolved in warm water 16.3L, and uniform solution was prepared. Furthermore, silica-sol 25kg whose silica content is 20wt(s)%, and 6.16kg of oxalic acid niobium ammonium solution whose concentration of niobium is 0.435 mols/kg were mixed, and the slurry was prepared. Having supplied this slurry to the spray drier the speed for about 120ml/, and supplying the heated air, moisture was removed and it dried. At this time, the temperature for a core of a spray drier was about 160 degrees C.

[0036] After heat-treating this dry matter at about 300 degrees C until the ammonia smell was lost, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The reactor was filled up with 1.0g of metallic oxides prepared as mentioned above, the reaction temperature of 410 degrees C and space velocity SV were fixed to 440hr<sup>-1</sup>, gas was supplied by the mole ratio of propane:ammonia:air = 1:1.2:15, and the gaseous-phase catalytic-oxidation reaction was performed. A reaction result is shown in Table -1.

[0037] 100g of 95 % of the weight oxalic acid solution of examples was warmed at 65 degrees C, and it prepared in the example 4 of comparison here -- it held at 65 degrees C for 1.5 hours, stirring by adding 10g (weight ratio 50:50) of  $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$  mixture of On and  $\text{SiO}_2$ . After cooling radiationally to a room temperature, filtration separation of the solid-state was carried out from this liquid. This solid-state was moved to another container, and 100ml of deionized water was added, and at the room temperature, it stirred for 5 minutes and filtered. Furthermore, this washing operation was repeated 3 times. After drying at a room temperature, it calcinated at 600 degrees C among the nitrogen air current for 2 hours. The gaseous-phase catalytic-oxidation reaction was performed for a propane and ammonia on the same conditions as the example 4 of comparison using the metallic oxide which performed the above processing. A reaction result is shown in Table -1.

[0038]

[Table 1]

表-1

	プロパン 転化率 (%)	アクリロニトリル 選択率 (%)	アクリロニトリル 収率 (%)
比較例 1	74.8	55.5	41.5
実施例 1	86.3	62.7	54.2
比較例 2	56.7	30.1	17.1
実施例 2	88.6	55.0	48.8
実施例 3	89.2	57.8	51.5
実施例 4	98.0	49.7	48.7
実施例 5	75.2	57.2	43.0
実施例 6	90.3	51.8	46.8
実施例 7	77.8	50.8	39.5
実施例 8	73.1	55.6	40.7
比較例 3	72.1	45.5	32.8
実施例 9	94.7	55.2	52.3
比較例 4	54.1	39.5	21.4

[0039]

[Effect of the Invention] According to this invention, since a metal oxide catalyst effective in the gaseous-phase catalytic-oxidation reaction of a hydrocarbon is more activable, acrylonitrile is useful as an industrial raw material, an acrylic acid, an anhydrous mallein, etc. can be manufactured by high yield.

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[Translation done.]